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THERMOELECTRIC PROPERTIES OF PLATINUM-RHODIUM ALLOYS

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ABSTRACT

The thermal electromotive forces and thermoelectric powers of a series of platinum-rhodium alloys against pure platinum have been determined from 0° to 1,200° C. The results obtained are compared with those obtained by other investigators.

The specimens used in this work contained the following percentages of rhodium, 0.100, 0.500, 1.000, 5.00, 21.6, 39.0, 51.6, 56.6, 61.2, 80.7, and 100.00.

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I. INTRODUCTION

The thermoelectric properties of the series of platinum-rhodium alloys are of more than incidental interest. In the first place it has become an almost universal practice to express the thermoelectric properties of substances in terms of their thermal electromotive forces or thermoelectric powers against pure platinum. Secondly, the thermal electromotive force of the platinum versus 90 per cent platinum-10 per cent rhodium thermocouple serves to define the International Temperature Scale [1] in the range 660° to 1,063° C. Furthermore, platinum to platinum-rhodium thermocouples of higher rhodium content are frequently used in thermoelectric temperature measurements.

Several observers have reported measurements of the thermoelectromotive forces of the platinum-rhodium alloys against pure platinum. The principal data are those of Holborn and Wien, 1892,[2] for rhodium contents of 9,10, 11, 15, 20, 30, 40, and 100 per cent; Holborn and Day, 1899,[3] for pure rhodium; Day and Sosman, 1909,[4] for 10 and 20 per cent rhodium; Sosman, 1910,[5] for a series of alloys containing from 1 to 20 per cent rhodium; Waidner and Burgess, 1907,[6] for 10 and 20 per cent rhodium. In addition to the values determined by himself, Sosman [5] included a summary of the results of previous observers who had used the higher percentages of rhodium.

[1] G. K. Burgess, International Temperature Scale, B. S. Jour. Research, vol. 1, p. 635, 1928.
[2] Holborn and Wien, "Uber die Messung hoher Temperaturen," Annalen der Physik, vol. 47, pp. 107-134, 1892.
[3] Holborn and Day, Thermoelectricity in Certain Metals, Am. J. Sci. (4), vol. 8, pp. 303-308, 1899.
[4] Day and Sosman, The Nitrogen Thermometer from Zinc to Palladium, Am. J. Sci (4), vol. 29, p. 119, 1910.
[5] Sosman, The Platinum-Rhodium Thermoelement, Am. J. Sci. (4), vol. 30, p. 1, 1910.
[6] Waidner and Burgess, The Melting Points of Palladium and Platinum, B. S. Bull., vol. 3, p. 200, 1907.

The values given by him have been used for comparison between the values given later in this paper and those of other observers.

In 1914 Adams [7] published a table giving the corresponding values of temperature and thermal electromotive force for the 90 per cent platinum-10 per cent rhodium alloy against platinum. This table has served for nearly 20 years as the standard of reference for this type of thermocouple.

While in some cases there is good agreement between the values obtained by different observers, such seems to be the exception rather than the rule. Accordingly, when rhodium and platinum-rhodium alloys of exceptionally high purity were produced in the course of the work on the purification of the platinum metals at the Bureau of Standards, it appeared desirable to redetermine the thermoelectric properties of these materials.

II. MATERIALS AND METHODS USED

Eleven alloys were used in this work, the rhodium contents as determined by analysis being 0.100, 0.500, 1.000, 5.00, 21.6, 39.0, 51.6, 56.6, 61.2, 80.7, and 100.00 per cent. There seemed to be no reason for determining the thermal electromotive force of a particular sample of a 10 per cent rhodium alloy prepared expressly for this work, since a wealth of data on this alloy has been collected at the Bureau of Standards as a result of years of routine calibrations of standard thermocouples. The values given for the 10 per cent rhodium alloy are very close to the values to be found in the table prepared by Adams.[8]

A platinum-10 per cent rhodium thermocouple, designated as D–3 was used for temperature determinations. This thermocouple was calibrated at the freezing points of gold, silver, and antimony in accordance with the International Temperature Scale,[9] and in addition at the freezing points of zinc, lead, and tin and the boiling point of water in order to extend its range to 0° C. The thermal electromotive forces of the alloys against the platinum element of D–3 were measured and corrections applied for the differences between this platinum and the sample of spectroscopically pure platinum used at the Bureau of Standards as the standard of purity.

In this connection it may be pointed out that the thermoelectric properties of a sample of platinum are a more sensitive indication of purity than even spectroscopic tests. The smallest amount of impurity which has been detected spectroscopically in platinum corresponds to a change in the thermal electromotive force of about 20 μv at 1,200° C. In some cases, depending upon the impurities present, the thermal electromotive force against the standard platinum has been found to be as much as 50 μv at 1,200° C., when spectroscopic tests failed to show any impurity.

In general, small amount of impurities usually found in platinum make it positive thermoelectrically to pure platinum. Every sample of platinum ever tested thermoelectrically at the Bureau of Standards, with one exception, has been found to be positive to Pt 27, the

[7] Adams, Calibration Tables for Copper-Constantan and Platinum-Platinrhodium Thermoelements, J. Am. Chem. Soc., vol. 36, p. 65, 1914. Interna. Critical Tables, vol. 1, p. 57, 1926. B. S. Tech. Paper, No. 170, p. 308, 1921.

[8] See footnote 7.

[9] See footnote 1, p. 373.

platinum standard of this bureau. This exception was a particular sample which was negative to the standard by only 2 μv at 1,200° C. For all practical purposes such a difference may be disregarded, and the two samples have been considered to be of equal purity. The platinum produced for thermocouples at the Bureau of Standards runs consistently purer than 0.99999; and it is probable that Pt 27, selected from this material for its exceptionally high purity, contains less than 1 part in 10^6 of impurity.

The method used in obtaining the values of thermal electromotive force of the alloy versus the platinum of thermocouple D–3 is similar to that used in the routine calibrations of thermocouples. Each alloy wire was heated electrically to about 1,500° C. and was held at this temperature for a few minutes after which it was fused to the hot junction of thermocouple D–3.

The thermocouple and alloy wires, in suitable insulating and protection tubes, were inserted in a chromel tube furnace whose temperature may be varied by small steps over the range from room temperature to 1,200° C. The thermocouple was connected to one potentiometer, and the platinum element of the thermocouple and the alloy wire were connected to another, each potentiometer having its own reflecting galvonometer. The connections were made through a cold junction bottle maintained at 0° C. The two lines of light from the galvanometers were thrown on the same scale, the galvanometers and light sources being so adjusted that on open circuit both lines of light came to rest on zero. The potentiometer connected to the standard thermocouple was set on the value of electromotive force corresponding to 50° C. and the temperature of the furnace was slowly increased. While the temperature was rising, the two lines of light on the scale were made to coincide as they crossed the zero of the scale by manipulation of the slide wire of the potentiometer connected to the alloy wire and platinum element of D–3. The potentiometer reading at this instant gave the electromotive force of the alloy against the platinum of the standard thermocouple at 50° C. This process was repeated at temperature intervals of 50° up to 1,150° C. The temperature of the furnace was then slowly reduced, and similar observations made. The means of the values obtained with increasing and decreasing temperatures were used and values at 1,200° C. were obtained by extrapolation.

The thermal electromotive force of the platinum wire of D–3 versus the platinum standard Pt 27 was determined several times during the series of determinations in the same manner. These values were added to those obtained for the alloy versus the platinum of D–3 to obtain the thermal electromotive force against Pt 27.

The furnace used consists of a chromel tube about 53 cm long, open at both ends, clamped between two water-cooled terminals. This tube is in the secondary circuit of a transformer whose primary voltage can be varied from 11 to 220 volts in steps of 11 volts. The temperature gradients at the ends of the tube are sharp, and the temperature is sensibly uniform over the middle portion of the tube. This uniform temperature distribution and sharp gradient make it possible to test the homogeneity of the materials by changing the depth of immersion of the thermocouple and alloy in the furnace. Measurements on all alloys used were made at several depths of immersion without detecting any inhomogeneity.

III. RESULTS

The results of measurements on the alloys actually used are given in Tables 1 and 2. Curves, shown in Figure 1 have been drawn from the data in these tables. Table 3, the data in which were obtained from these curves, will probably be found more convenient for interpolation than Table 2. The values of Tables 1 and 3 are plotted in Figure 2. The thermoelectric powers obtained from the values of Tables 1 and 3 are plotted as functions of temperature in Figure 3.

The observations at a given temperature taken with increasing and decreasing temperature in no case differed by more than 6μv, and in general the difference ranged from 0 to 3μv. The mean of these two values at a given temperature never differed more than 3μv from the

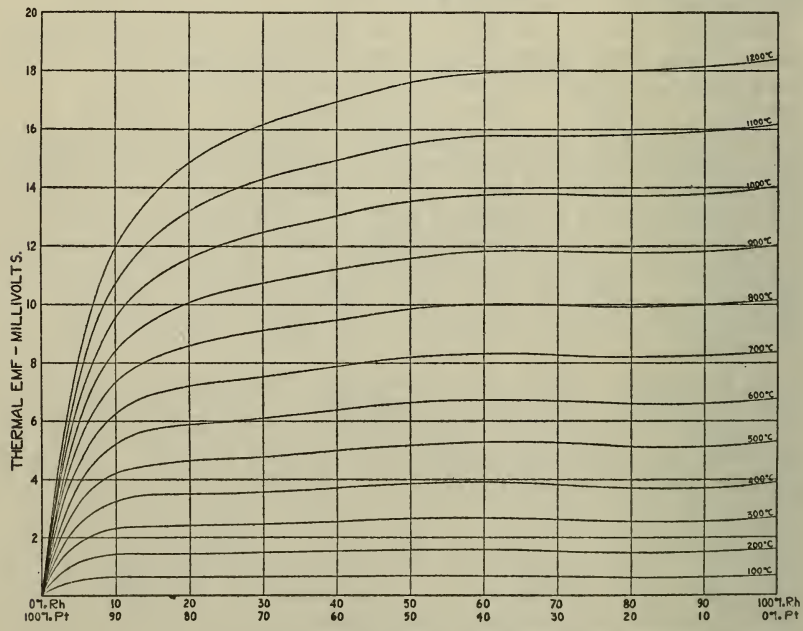

FIGURE 1.—*Thermal electromotive force of platinum-rhodium alloys against platinum plotted against composition*

corresponding means obtained at different times and at different depths of immersion. The values reported are given in terms of the international volt and include potentiometer corrections and the correction to convert the actual observations to thermal electromotive forces versus Pt 27.

While it is believed that the measurements of electromotive force are accurate to about 3μv, the tabulated results expressing electromotive force as a function of composition can not be considered as accurate as this at the higher temperatures on account of uncertainties in chemical analyses. For the analyses given, the values at the higher temperatures are not considered accurate to better than 5μv for the 0.1 and 0.5 per cent rhodium 10μv for the 1 and 100 per cent rhodium, 40μv for the 20 per cent rhodium and 20μv for the other alloys.

TABLE 1.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum for compositions containing 0.1 to 10.0 per cent rhodium*

Temperature	Per cent rhodium				
	0.1	0.5	1.0	5.0	10.0
° C.					
50	+0.009	+0.049	+0.088	+0.255	+0.298
100	.020	.097	.180	.536	.643
150	.031	.146	.275	.837	1.025
200	.042	.195	.372	1.154	1.436
250	.053	.245	.471	1.479	1.867
300	.065	.294	.568	1.809	2.315
350	.076	.343	.663	2.143	2.777
400	.087	.391	.758	2.479	3.249
450	.098	.438	.852	2.816	3.730
500	.109	.484	.945	3.155	4.218
550	.119	.530	1.037	3.494	4.715
600	.130	.576	1.128	3.835	5.221
650	.140	.621	1.219	4.177	5.737
700	.150	.666	1.309	4.520	6.260
750	.161	.711	1.398	4.866	6.791
800	.171	.756	1.489	5.216	7.331
850	.181	.802	1.579	5.569	7.879
900	.192	.847	1.669	5.924	8.435
950	.202	.892	1.760	6.282	8.998
1,000	.213	.937	1.852	6.643	9.570
1,050	.223	.982	1.943	7.007	10.149
1,100	.233	1.028	2.034	7.375	10.737
1,150	.244	1.073	2.126	7.746	11.329
1,200	.254	1.118	2.218	8.121	11.922

TABLE 2.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum for compositions containing 20 to 100 per cent rhodium*

Temperature	Per cent rhodium						
	21.6	39.0	51.6	56.6	61.2	80.7	100.0
° C.							
50	+0.280	+0.295	+0.306	+0.304	+0.298	+0.276	+0.314
100	.620	.651	.682	.676	.672	.623	.696
150	1.010	1.060	1.115	1.109	1.105	1.028	1.127
200	1.443	1.515	1.596	1.592	1.590	1.492	1.606
250	1.913	2.011	2.119	2.120	2.120	2.002	2.128
300	2.415	2.543	2.678	2.685	2.687	2.554	2.687
350	2.945	3.107	3.268	3.286	3.288	3.144	3.282
400	3.500	3.700	3.888	3.914	3.920	3.770	3.915
450	4.077	4.322	4.537	4.577	4.582	4.430	4.580
500	4.675	4.972	5.215	5.266	5.275	5.122	5.281
550	5.294	5.650	5.922	5.982	5.997	5.846	6.010
600	5.936	6.356	6.657	6.732	6.747	6.602	6.772
650	6.599	7.085	7.419	7.505	7.525	7.389	7.566
700	7.282	7.847	8.207	8.307	8.331	8.206	8.398
750	7.984	8.633	9.024	9.134	9.165	9.053	9.262
800	8.702	9.446	9.869	9.996	10.028	9.931	10.158
850	9.443	10.286	10.742	10.885	10.922	10.839	11.085
900	10.201	11.152	11.645	11.797	11.844	11.777	12.043
950	10.977	12.043	12.577	12.741	12.795	12.746	13.034
1,000	11.771	12.960	13.538	13.714	13.776	13.745	14.050
1,050	12.582	13.902	14.526	14.711	14.785	14.773	15.100
1,100	13.411	14.870	15.540	15.737	15.822	15.830	16.181
1,150	14.257	15.862	16.580	16.787	16.890	16.914	17.292
1,200	15.121	16.876	17.646	17.863	17.986	18.024	18.432

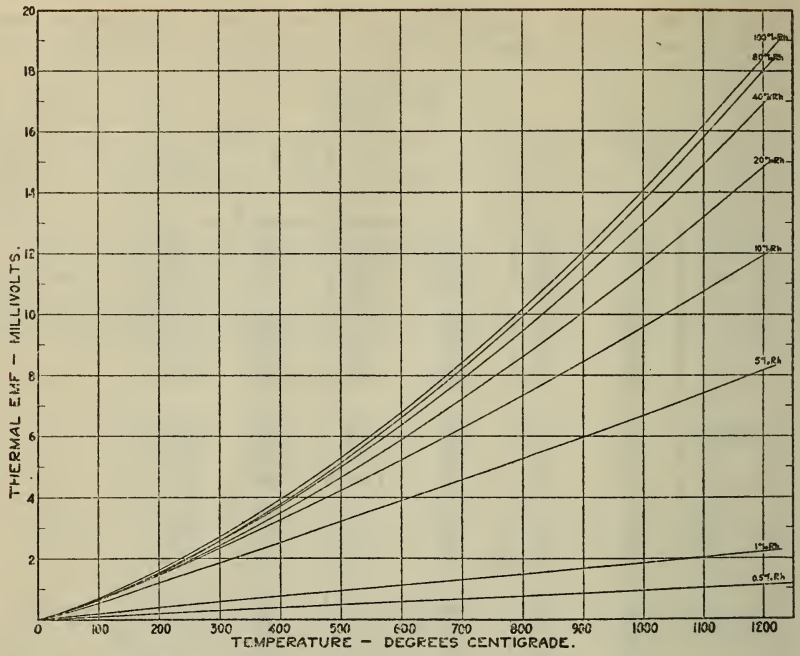

FIGURE 2.—*Thermal electromotive force of platinum-rhodium alloys against platinum plotted against temperature*

TABLE 3.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum, adjusted values*

Temperature	Per cent rhodium						
	20.0	40.0	50.0	55.0	60.0	80.0	100.0
° C.							
100	+0.63	+0.65	+0.68	+0.68	+0.67	+0.62	+0.70
200	1.44	1.52	1.59	1.59	1.59	1.49	1.61
300	2.40	2.55	2.67	2.69	2.68	2.55	2.68
400	3.47	3.70	3.87	3.90	3.92	3.77	3.91
500	4.63	4.97	5.19	5.24	5.27	5.12	5.28
600	5.87	6.36	6.62	6.70	6.74	6.60	6.77
700	7.20	7.85	8.17	8.27	8.32	8.20	8.40
800	8.59	9.45	9.82	9.95	10.02	9.92	10.16
900	10.06	11.16	11.59	11.75	11.83	11.76	12.04
1,000	11.58	12.98	13.47	13.65	13.76	13.73	14.05
1,100	13.17	14.90	15.46	15.66	15.80	15.81	16.18
1,200	14.84	16.91	17.56	17.79	17.94	17.99	18.42

From the values given in Table 1 it can be seen that the thermal electromotive force does not always increase with rhodium content, and that some of the curves of Figure 2, obtained by adjusting the values of Tables 1 and 2 for even percentages cross at the lower temperatures. This result agrees in general with the determinations of previous observers.

Referring to Figure 1, it will be noted that the curves exhibit fairly definite maxima in the region of 60 per cent rhodium. Since the alloy containing 56.6 per cent rhodium was the only one in the original group whose rhodium content was within the range 40 to 80 per cent,

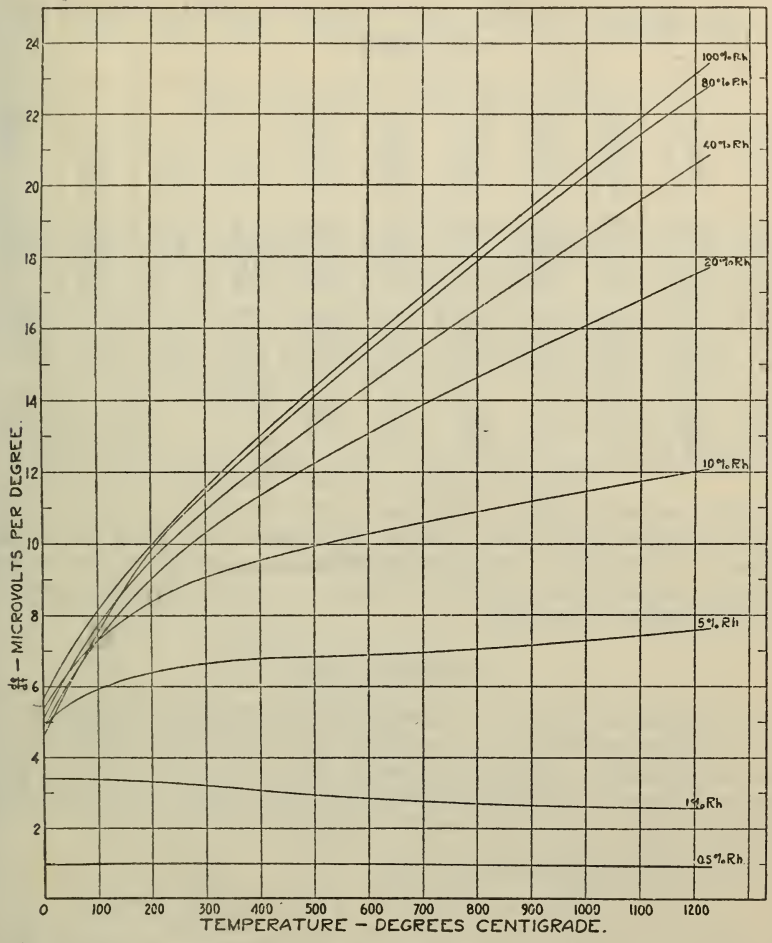

FIGURE 3.—*Thermoelectric power of platinum-rhodium alloys against platinum plotted against temperature*

it was thought desirable to check the data obtained with this alloy. This was done by preparing two additional alloys containing 51.6 and 61.2 per cent rhodium. The data obtained with these additional alloys confirmed the data previously obtained with the 56.6 per cent rhodium alloy.

TABLE 4.—*Thermal emf of pure platinum against platinum-rhodium alloys, in millivolts*

[Reproduced from Sosman's paper]

t	1 per cent	5 per cent	10 per cent			15 per cent	20 per cent	30 per cent	40 per cent	100 per cent
			Low	High	Standard					
	°C.									
100	0.21	0.55	0.63	0.64	0.64	0.65				0.65
200	.42	1.18	1.41	1.43	1.43	1.50				1.51
300	.63	1.85	2.28	2.32	2.32	2.41		2.34	2.45	2.57
400	.84	2.53	3.21	3.26	3.25	3.45	3.50	3.50	3.64	3.76
500	1.05	3.22	4.17	4.23	4.23	4.55	4.60	4.74	4.93	5.08
600	1.25	3.92	5.16	5.24	5.23	5.71	5.83	6.06	6.31	6.55
700	1.45	4.62	6.19	6.28	6.27	6.94	7.18	7.49	7.80	8.14
800	1.65	5.33	7.25	7.35	7.33	8.23	8.60	9.01	9.37	9.87
900	1.85	6.05	8.35	8.46	8.43	9.57	10.09	10.67	11.09	11.74
1,000	2.05	6.79	9.47	9.60	9.57	10.96	11.65	12.42	12.94	13.74
1,100	2.25	7.53	10.64	10.77	10.74	12.40	13.29	14.33	14.99	15.87
1,200	2.45	8.29	11.82	11.97	11.93	13.87	14.96	16.39	17.13	18.10
1,300	2.65	9.06	13.02	13.18	13.13	15.38	16.65	18.51	19.51	20.46
1,400	2.86	9.82	14.22	14.39	14.34	16.89	18.39	20.67	21.73	
1,500	3.06	10.56	15.43	15.61	15.55	18.41	20.15			
1,600	3.26	11.31	16.63	16.82	16.75	19.94	21.90			
1,700	3.46	12.05	17.83	18.03	17.95	21.47	23.65			
1,755	3.56	12.44	18.49	18.70	18.61	22.31	24.55			

Table 4, reproduced from Sosman's paper is inserted here for comparison between the values given in this paper and those previously obtained. It will be seen that the differences between the present values and those summarized by Sosman are relatively small, and are not consistently of one sign.

IV. SUMMARY

The thermal electromotive forces and thermoelectric powers of a series of platinum-rhodium alloys have been determined against pure platinum from 0° to 1,200° C. Comparisons are made between these values and those obtained by several other investigators, the maximum difference found being of the order of 300 μv.

WASHINGTON, December, 14, 1932.